

**Physicochemical properties of 1,2,4-triazolium
perfluorobutanesulfonate as an archetypal pure protic
organic ionic plastic crystal electrolyte**

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High temperature polymer electrolyte membrane fuel cells (PEMFCs) operating between 100 °C and 200 °C are desirable because they offer significant benefits, such as improved electrode kinetics, simpler water and heat management, and better tolerance to fuel impurities, leading to higher overall system efficiencies [1]. However, state-of-the-art high temperature PEMFCs suffer from leakage problems associated with liquid electrolytes, such as H₃PO₄ and protic ionic liquids [2,3].

Recently, organic ionic plastic crystals (OIPCs), which are unique electrolyte materials due to their superior properties such as intrinsic ionic conductivity, non-flammability, negligible vapor pressure, plasticity, high thermal stability, and wide electrochemical window [4–7], are promising for the realization of all-solid-state PEMFCs [6,7]. While the OIPCs used as electrolytes for PEMFCs should be proton-conducting, they are often doped plastic crystals, which employ acids, protic ionic liquids or bases as the dopants for doping the matrix of certain neat plastic crystals [8–10].

In order to obviate the use of dopants that may be incompatible with the host matrix of plastic crystals, we have developed some highly proton-conductive pure plastic crystals that are protic OIPCs, as they are protic molten salts when they are in the liquid state [2]. Here, we present our recent work on 1,2,4-triazolium perfluorobutanesulfonate (**1**) as a model proton conductor for high temperature PEMFCs.

Firstly, **1** (Fig. 1) was synthesized by mixing equimolar amounts of 1*H*-1,2,4-triazole and perfluorobutanesulfonic acid (CF₃CF₂CF₂CF₂SO₃H), followed by heating at 190 °C for 2 h to promote the complete formation of the organic salt. **1** was purified by evacuating in a Schlenk line at 190 °C for 12 h to eliminate water and the excess base or acid. Infrared spectra confirmed the formation and purity of the organic salt. Thermogravimetric analysis and isothermal gravimetric analysis showed the superior thermal stability of **1**. Differential scanning calorimetry (DSC) of **1** in the form of both fine powders and pellets showed two solid-solid phase transitions at 77 °C and 87 °C, respectively, wherein only the latter seemed to be reversible. At the

melting point of 181 °C, **1** exhibited an entropy of fusion (ΔS_f) of 46.0 J mol⁻¹ K⁻¹, which falls in the normal range of ΔS_f values for OIPCs [4]. Temperature-dependent X-ray diffraction (XRD) tests confirmed the two solid-solid phase transitions. Thermomechanical analysis further confirmed the DSC and XRD results while polarized optical microscopy excluded the possibility of partial melting at 77 °C and 87 °C. The wide temperature range for the plastic phase between 87 °C and 181 °C is ideal for the application of **1** in high temperature PEMFCs. Single crystals of **1** were grown by the vapor diffusion method. Single-crystal X-ray crystallography was performed successfully at 100 K and 300 K, which revealed the molecular structure of **1** and its strong N–H···O hydrogen bonding network. Scanning electron microscopy was employed to observe the morphology of **1** at different temperatures. Temperature-dependent Raman spectra were recorded to study the N–H bond and hydrogen bonding of **1** and 1*H*-1,2,4-triazole at various temperatures. The temperature dependence of the ionic conductivity of **1** was measured by electrochemical impedance spectroscopy (conductivity spectroscopy), showing an ionic conductivity higher than 1 Ω⁻¹ m⁻¹ at 185 °C. In terms of fuel cell applications, the open circuit voltage (OCV) tests for H₂/air single fuel cells using pellets of **1** showed a high OCV of 1.05 V at 50 °C. Furthermore, the measurement of high temperature PEMFC performance of an inert membrane matrix hosting **1** will be carried out soon.

In conclusion, as a pure protic OIPC, **1** is a promising anhydrous proton conductor for the realization of an all-solid-state high temperature PEMFC.

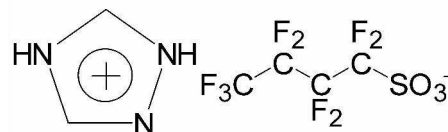


Fig. 1 Chemical structure of the proton conductor **1**.

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